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INDUCED INFRARED ABSORPTION IN GASEOUS ACETYLENE AT PRESSURE, III

BY SHIGERU MINOMURA

Introduction

In the previous papers¹⁾ the pressure-induced absorption of totally symmetric fundamental ν_2 at 1974 cm^{-1} of acetylene for the pure gas at the pressure up to 24 kg/cm^2 and the mixtures with the foreign gases (nitrogen, argon, or hydrogen) at the total pressure up to 100 kg/cm^2 has been investigated and the following results obtained. For acetylene the integrated absorption coefficient ($\text{sec}^{-1}/\text{cm}/\text{Amagat C}_2\text{H}_2$) increases linearly with increasing density. For the mixtures the integrated absorption coefficient of the enhancement by the addition of the foreign gas ($\text{sec}^{-1}/\text{cm}/\text{Amagat C}_2\text{H}_2/\text{Amagat foreign gas}$) increases linearly with increasing density of the foreign gas. The absorption coefficients both for acetylene and the mixtures increase linearly with increasing temperature. The magnitude of the absorption coefficients and their temperature coefficients increase with increasing molecular polarizability²⁾, $\text{C}_2\text{H}_2 > \text{N}_2 > \text{A} > \text{H}_2$. The induced ν_2 -band for acetylene consists of two sub-branches which indicate the maximum absorptions at 1944 and 2009 cm^{-1} , corresponding to the rotational transitions $\Delta J = -1$ and $+1$, respectively, where J is the rotational quantum number of the acetylene molecule. The fact is consistent with the hypothesis that the molecules behave momentarily as the rigid rotator with a dipole moment perpendicular to the axis of rotation, which is caused by the distortion of the electronic charge distribution of the molecules during collision. The rate of change $\partial\mu/\partial R$ of the induced dipole moment μ with $\text{C}\equiv\text{C}$ bond length R , which is obtained from the integrated absorption coefficient, is $\pm 0.2 \times 10^{10}$ (c. g. s. units) for 10 Amagat of acetylene. The value is of the same order as that with the $\text{C}-\text{H}$ bond which contributes to the infrared active fundamentals of acetylene. The induced ν_2 -band for the mixtures of acetylene with the foreign gases shows not only the enhancement of the two sub-branches described above, but also that of the sub-branch at the band origin, 1974 cm^{-1} , corresponding to $\Delta J = 0$.

In the present investigation carbon dioxide which is of the magnitude of molecular polarizability between acetylene and nitrogen has been used as the foreign gas and the effect of the foreign gas on the induced ν_2 -band of acetylene has been studied

1) R. Kiyama, S. Minomura and K. Ozawa, *Proc. Japan Acad.*, **30**, 758 (1954)
S. Minomura, *This Journal*, **24**, 49 (1955), **26**, 9 (1956)

2) J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, *Molecular Theory of Gases and Liquids*, John Wiley & Sons, Inc., New York, p. 950 (1954)

and compared with the effect of nitrogen.

On the other hand, for carbon dioxide and the mixture with acetylene the pressure-induced absorptions^{3,4)} of the totally symmetric fundamental ν_1 at 1388 cm^{-1} and the first overtone $2\nu_2^0$ at 1286 cm^{-1} , which are in Fermi resonance⁵⁾, have been studied and the absorption coefficients at both frequencies discussed.

Experimentals

The absorption cell and the infrared spectrometer used in this investigation have been described in the previous papers¹⁾. A crystal of lithium fluoride was used as the cell window in the spectral measurement of the induced absorption in acetylene and substituted by a crystal of potassium chloride for admitting the transmission of light in that of the induced absorption in carbon dioxide. The path lengths were 16.6 and 16.7 cm, respectively.

The purification of gaseous acetylene from calcium carbide and water was performed by the same method as described in the previous papers and the absorption bands contributed to the impurities were not observed in the frequency range of the induced ν_2 -band of acetylene. Compressed gaseous carbon dioxide distilled from the liquid in a commercial bomb was used. The Amagat densities under the experimental conditions were calculated from the pressure-volume-temperature data cited in the literatures^{1,6)}. It was assumed for gaseous mixtures that the density of each gas could be calculated from the partial pressure. The absorption in nitrogen at the atmospheric pressure was determined as a back ground for the spectra of pure gas and the absorption in the foreign gas at the partial pressure for the spectra of the mixtures.

Results and Discussions

The induced ν_2 -band for the mixtures of acetylene of 5.4 and 11.0 Amagat with carbon dioxide up to 20 Amagat is shown in Fig. 1. The spectra indicate five sub-maxima at 1944, 1974, 2009, 2110 and 2189 cm^{-1} . The remarkable enhancement of the absorption is brought about in the band tail of the high frequency side, in comparison with that for the mixture of acetylene with nitrogen, which has been observed in the previous papers. It is ascribed to the broadening effect of the infrared active fundamental at 2349.3 cm^{-1} of carbon dioxide by acetylene. The frequency of 1974 cm^{-1} accords with the band origin of the fundamental ν_2 of acetylene, and the frequencies of 1944 and 2009 cm^{-1} accord with the two sub-maxima for acetylene. Two sub-

3) H. L. Welsh, M. F. Crawford and J. L. Locke, *Phys. Rev.*, **76**, 580 (1949)

4) J. Fahrenfort, *Chemisch Weekblad*, **50**, 501 (1954)

5) E. Fermi, *Z. Phys.*, **71**, 250 (1931)

6) F. Din, *Thermodynamic Functions of Gases*, Butterworths Scientific Publications, London, Vol. 1, p. 102 (1956)

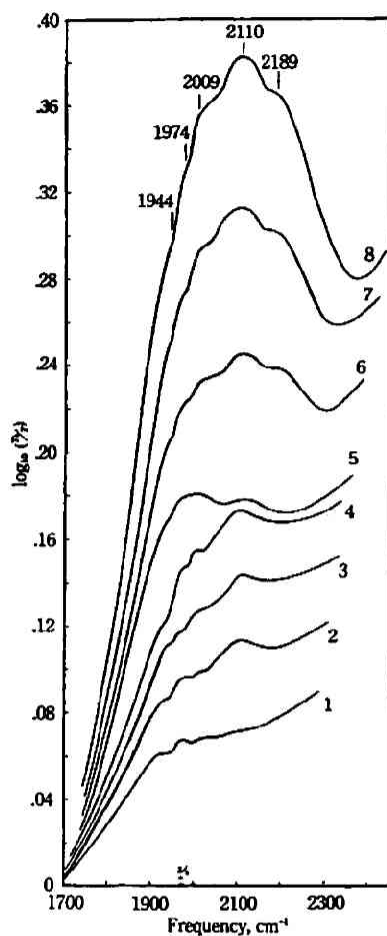


Fig. 1 The enhancement of the induced absorption in acetylene by the addition of carbon dioxide

curve 1	5.4 Amagat C_2H_2 + 1.0 Amagat CO_2
2	" + 6.4 "
3	" + 12.8 "
4	" + 19.6 "
5	11.0 Amagat C_2H_2 + 1.0 Amagat CO_2
6	" + 6.6 "
7	" + 12.8 "
8	" + 20.0 "

maxima at 2110 and 2189 cm^{-1} are remarkable with increasing densities of acetylene and carbon dioxide. They have not been observed in the case of the mixture of acetylene with nitrogen, argon, or hydrogen in the previous papers.

The integrated absorption coefficient of the enhancement of the induced ν_2 -band of acetylene by the addition of the foreign gas is of the form¹⁾,

$$\int (a - a_0) d\nu = a_1 \rho_f + a_2 \rho_f^2, \quad (1)$$

where a_0 and a are the absorption coefficients for acetylene and the mixture with the foreign gas ($cm^{-1}/Amagat C_2H_2$), ν frequency, ρ_f the density of the foreign gas, and a_1 and a_2 constants. Because the spectra for the mixture of acetylene with carbon dioxide in Fig. 1 do not show the complete splitting of the induced ν_2 -band to give the integrated absorption coefficient, assuming that $\int (a - a_0) d\nu$ can be substituted by the absorption coefficient of the enhancement, $(a - a_0)_{2009}$, at 2009 cm^{-1} which is one of two sub-maxima of the induced ν_2 -band for acetylene,

$$(a - a_0)_{2009} = a_1 \rho_f + a_2 \rho_f^2. \quad (2)$$

Eq. (2) expresses that a plot of $1/\rho_f(a - a_0)_{2009}$ ($cm^{-1}/Amagat C_2H_2/Amagat$ foreign

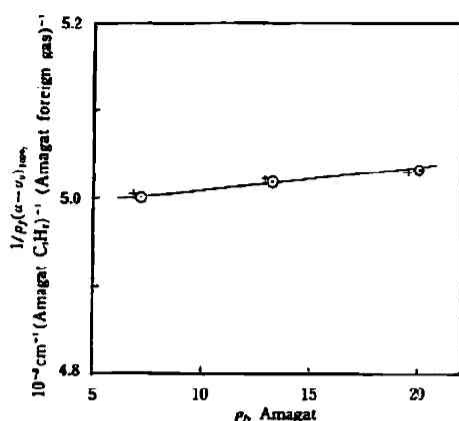


Fig. 2 The relation between the induced absorption coefficient of acetylene at 2009 cm^{-1} and the density of foreign gas, ρ_f

+ 11.0 Amagat C_2H_2
 ○ 5.4 "

gas) against ρ_f shows a straight line, as in Fig. 2. The constant a_1 is equal to the value of the ordinate which is obtained by the extrapolation of the straight line in Fig. 2 to zero density of the foreign gas. The constant a_2 is given from the slope of the straight line. The values of a_1 and a_2 are compared with those determined for acetylene-nitrogen mixture⁷⁾ in Table 1. The values of a_1 and a_2 for carbon dioxide are much larger than those for nitrogen.

Table 1 The absorption coefficients of the induced ν_2 -band of acetylene for the mixtures with carbon dioxide and nitrogen

Foreign gas	Density of acetylene Amagat	Absorption coefficients	
		a_1 $\text{cm}^{-1}/\text{Amagat C}_2\text{H}_2/ \text{Amagat foreign gas}$	a_2 $\text{cm}^{-1}/\text{Amagat C}_2\text{H}_2/ (\text{Amagat foreign gas})^2$
Carbon dioxide	11.0	50×10^{-6}	26×10^{-9}
	5.4		
Nitrogen	9.4	2.6×10^{-6}	5.0×10^{-9}
	4.6		

The pressure-induced absorption in carbon dioxide at four densities up to 14.3 Amagat in the frequency range of 1200~1500 cm^{-1} is shown in Fig. 3. The spectra indicate five maxima at 1265, 1286, 1335, 1388 and 1410 cm^{-1} , which are infrared inactive at the atmospheric pressure and Raman active⁷⁾. The bands at 1388 and 1286 cm^{-1} are brought about in consequence of the Fermi resonance between the totally symmetric fundamental ν_1 and the first overtone of perpendicular band ν_2 . The band at 1286 and 1335 cm^{-1} can be identified as two sublevels of $2\nu_2$, corresponding with the vibrational angular momentum $l=0$ and 2, respectively. The absorption coefficients at the both frequencies per unit Amagat carbon dioxide increase linearly with increas-

7) G. Herzberg, *Molecular Spectra and Molecular Structure*, Nostrand Co., Inc., New York, p. 274 (1945)

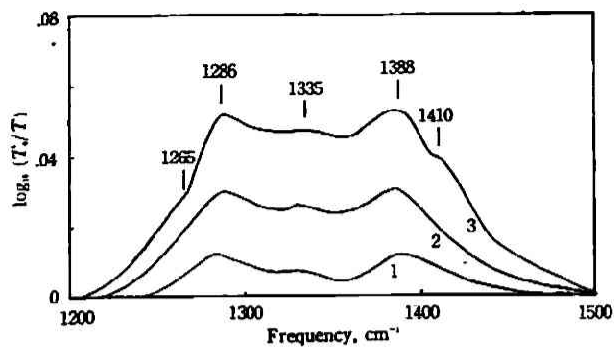


Fig. 3 The induced absorption in carbon dioxide at various densities

back ground	1.0 Amagat CO ₂
curve 1	4.1 "
2	9.1 "
3	14.3 "

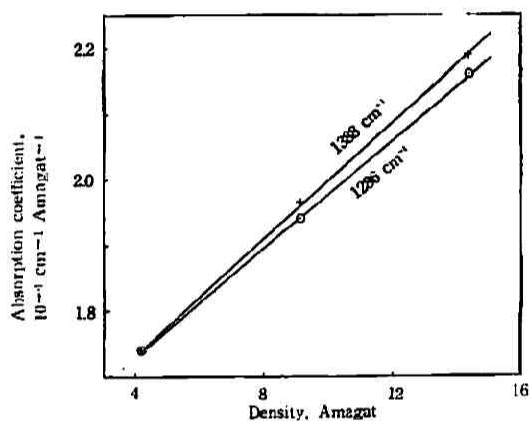
Fig. 4 The relation between the induced absorption coefficients of carbon dioxide at 1286 and 1388 cm⁻¹ and the density

Table 2 The induced absorption coefficients of carbon dioxide and acetylene

Perturbing gas	Band frequency cm ⁻¹	Assignment	Absorption coefficient cm ⁻¹ /Amagat ²
Carbon dioxide	1286	$2\nu_2^0$	4.2×10^{-6}
	1388	ν_1	4.6×10^{-6}
Acetylene	1974	ν_2	32×10^{-6}

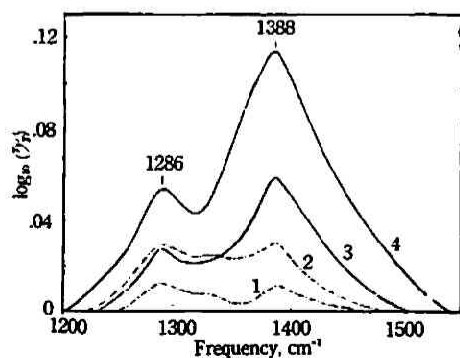


Fig. 5 The enhancement of the induced absorption in carbon dioxide by the addition of acetylene

curve 1	4.1 Amagat CO ₂
2	9.1 "
3	4.1 " +2.2 Amagat C ₂ H ₂
4	9.1 " +2.2 "

Table 3 The induced absorption coefficients of carbon dioxide for the mixture with acetylene

Density of CO ₂ Amagat	Density of C ₂ H ₂	Absorption coefficients cm ⁻¹ /Amagat CO ₂ /Amagat C ₂ H ₂	
		at 1286 cm ⁻¹	at 1388 cm ⁻¹
4.1	2.2	1.8×10^{-4}	3.7×10^{-4}
9.1	2.2	1.7×10^{-4}	3.5×10^{-4}

ing density, as shown in Fig. 4. The values (cm⁻¹/Amagat²) determined by the slope of the straight line in the diagram and that for the induced ν_2 -band at 1974 cm⁻¹ of acetylene observed in the previous paper are given in Table 2.

The induced absorption in carbon dioxide of 4.1 and 9.1 Amagat for the mixture with acetylene of 2.2 Amagat is shown in Fig. 5. The spectra show the remarkable enhancement of the absorptions at 1286 and 1388 cm⁻¹, in which the latter is much greater than the former. The absorption coefficients at the both frequencies per unit Amagat carbon dioxide and per unit Amagat acetylene are given in Table 3.

In consequence of the Fermi resonance, ν_1 and $2\nu_2^0$ give Raman bands of the intensities of the same order, whereas without resonance the fundamental would, in general, have much greater intensity than the overtone^{7, 8)}. The ratios of the absorption coefficients, $\alpha_{1286} : \alpha_{1388}$, between the pressure-induced absorption bands at 1286 and 1388 cm⁻¹ for carbon dioxide and the mixture with acetylene and the intensity ratios, $I_{1286} : I_{1388}$, between the Raman bands at their frequencies, which have been obtained by a number of investigators⁹⁻¹²⁾ for carbon dioxide at pressure are summarized in Table 4.

Table 4

For pressure-induced bands	$\alpha_{1286} : \alpha_{1388}$
Carbon dioxide	0.91 : 1
Carbon dioxide+acetylene	0.48 : 1
For Raman bands	$I_{1286} : I_{1388}$
From data of Dickinson, Dillon and Rasetti	10 : 15
" Bhagavantam	1 : 3
" Hanson	0.572 : 1
" Langseth and Nielsen	0.61 : 1

8) E. B. Wilson, J. C. Decius and P. C. Cross, *Molecular Vibrations*, McGraw-Hill Book Co., Inc., New York, p. 197 (1955)

9) R. G. Dickinson, R. T. Dillon and F. Rasetti, *Phys. Rev.*, **34**, 582 (1929)

10) S. Bhagavantam, *Nature*, **127**, 817 (1931)

11) I. Hanson, *Phys. Rev.*, **46**, 122 (1934)

12) A. Langseth and J. R. Nielsen, *ibid.*, **46**, 1057 (1934)

The pressure-induced absorption bands at 1286 and 1388 cm^{-1} for carbon dioxide have much the same intensity, in comparison with the relative intensities for the both Raman bands. For the mixture of carbon dioxide with acetylene the intensity of the pressure-induced band at 1388 cm^{-1} is about twice as much as that at 1286 cm^{-1} . That is, the addition of acetylene induces much greater dipole moment in C—O direction for carbon dioxide molecules, which contributes to the enhancement of the induced ν_1 -band at 1388 cm^{-1} , than that in the perpendicular direction, which contributes to the enhancement of the induced $2\nu_2^0$ -band at 1286 cm^{-1} .

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